

High Resolution Structural Studies of Porphyrin Radicals

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Beamline(s): X3A1

Introduction: Porphyrins are tetrapyrrole derivatives that mediate a spectrum of bioenergetic reactions ranging from photosynthetic solar energy transduction to conversion of carbon dioxide into fuel. Their structures have been widely studied to ascertain the factors that control bioenergetic and catalytic reactions [1]. Furthermore, oxidized metalloporphyrins are important intermediates in the catalytic cycles of heme proteins and in photosynthetic processes. In order to assess the stereochemical consequences of porphyrin oxidation, the structures of nonplanar model porphyrins that undergo facile one electron oxidation of the macrocycle to cation radicals have been examined. Changes in conformation that occur upon oxidation have been shown to alter the chemical and physical properties of porphyrin complexes and may dictate their reactivity in vivo [2]. Among the compounds investigated are two sterically encumbered Co(II) cation radicals and their neutral precursor.

Methods and Materials: All data were collected at 20K with a Bruker CCD detector at wavelength 0.643Å. The data were processed and merged with SAINT [3] and the structures were refined with the SHELXTL package [4].

Results: The molecular structure of one of the two new Co(II) porphyrin radicals is shown in Figure 1. Derived esds on the Co-N and Co-O distances are 0.001Å and on typical C-C bonds are 0.002Å. Final values of R1 and wR2 are 0.047 and 0.123 based on 21755 reflections measured to 0.47Å resolution [5].

Conclusions: These studies currently make it possible to ascertain the stereochemical consequences of oxidation at high resolution and high precision, and in the future will allow actual orbital occupancies of the metals and electron populations of the porphyrin atoms to be determined.

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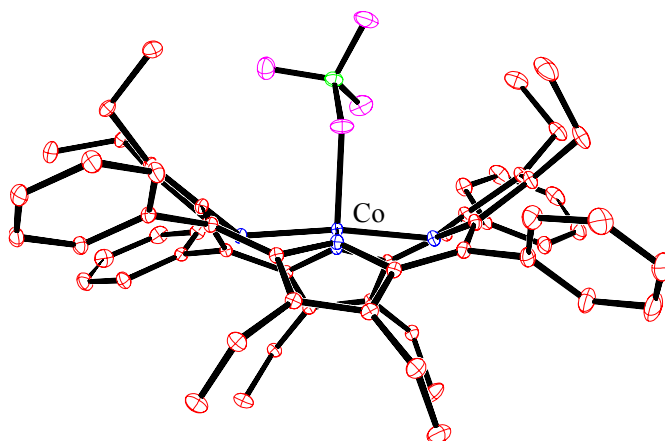


Figure 1. Edge-on view of the molecular structure of a Co(II) cation radical, which clearly illustrates the distorted conformation of the macrocycle and the perchlorate counterion that is bonded to the Co. It is significantly more distorted than its neutral precursor. Thermal ellipsoids are drawn at the 50% probability level.